Vacuum pressure swing adsorption oxygen for oxygen delignification

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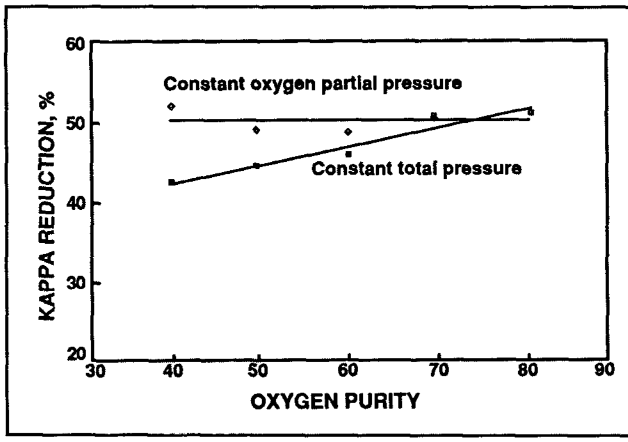
Oxygen of 90–93% purity, produced in on-site plants by the vacuum pressure swing adsorption method, may be the lowest cost form of oxygen for an oxygen delignification stage.

Oxygen is being used in large quantities to reduce chlorine consumption and bleaching costs. Most pulp mills purchase liquid oxygen delivered by truck from merchant air separation plants. As a mill consumes more oxygen, it becomes more economical to situate an oxygen-producing plant on site.

The conventional technology used to generate merchant and on-site oxygen is cryogenic distillation of air. This process produces oxygen of 99.5% purity.

An alternative on-site air separation technology that offers lower cost to meet volume requirements is vacuum pressure swing adsorption (VPSA). VPSA plants produce oxygen that is 90–93% pure oxygen on a pulp mill's oxygen delignification stage—the major consumer of oxygen in most mills. Here, we will look at theoretical evaluations and at results from two mill trials of the VPSA process.

1. Delignification vs. oxygen purity (softwood pulp, initial kappa no. 28.4, 1.8% NaOH, high consistency)



Oxygen by vacuum pressure swing adsorption

VPSA plants use molecular sieves to produce oxygen from air. Air is compressed and passed through a bed of synthetic zeolite, which adsorbs the nitrogen, carbon dioxide, and water vapor by forming a weak electrochemical bond on the surface of the sieve. Oxygen and argon are not attracted to the adsorbent and pass through to form the product. To regenerate the bed, the pressure is reduced, which releases the nitrogen and other trapped gases and allows them to be vented.

Zeolite sieves cannot differentiate between oxygen and argon. Since oxygen and argon are present in a ratio of roughly 20:1 in air, the highest oxygen purity that can be achieved with a VPSA system is 95%. Commercial systems are optimized to produce oxygen close to this purity, at 90–93%, with the remaining 7–10% being inert nitrogen and argon.

VPSA technology has improved in the past three years. The major advances are the development of more efficient vacuum cycles to regenerate the adsorbent beds and a new generation of advanced adsorbents. These developments have reduced the size of these plants and their capital costs. Power requirements have also dropped. VPSA plants now require less energy to generate a kilogram of oxygen than cryogenic distillation plants of the same size.

The oxygen requirements that can be supplied most economically with VPSA plants are between 15 and 130 metric tons per day. Below 15 tons/day, oxygen is most economically supplied by having bulk liquid oxygen trucked from a merchant air separation plant. Above 130 tons/day, large single-train cryogenic distillation plants offer better economics than the multi-train VPSA systems that would be required. The break points vary widely depending on the oxygen user's location, use pattern, power cost, and purity requirements.

If the purity is acceptable, VPSA oxygen supply is a suitable method of supply for a pulp mill. Typically, a 1000-tons/day softwood kraft mill uses 20–30 metric tons of oxygen per day for medium-consistency oxygen delignification and oxygen extraction bleaching. For softwood

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kraft pulp mills that have a steady use pattern and moderate pressure requirements and that are often located far from merchant air separation plants, VPSA oxygen offers savings over alternative supply methods.

Experience with the use of 90-93% pure oxygen for oxygen delignification is limited. A mill in Japan successfully uses oxygen of this purity in a high-consistency oxygen delignification stage (*1*). A hardwood mill in Taiwan has operated a medium-consistency oxygen delignification stage for two years with VPSA oxygen. Until mid-1990, no mill in North America, Europe, or South America has used VPSA for oxygen delignification, but this status is changing rapidly. Within one year, at least four mills in North America and other mills worldwide will use VPSA oxygen.

Theoretical evaluation

Three possible adverse effects were identified that could result from the use of VPSA oxygen in an oxygen delignification stage.

Partial pressure: The lower partial pressure of oxygen may limit the delignification or increase the oxygen requirement.

Gas volume: The extra gas volume may limit reactor capacity or cause channeling.

Post-oxygen washing: Carryover of inert gases to the post-oxygen washers may result in poor washing.

Partial pressure

The extent and rate of delignification in an oxygen delignification stage are proportional to the partial pressure of oxygen (*2*, *3*). Low-purity oxygen produces the same results as pure oxygen, provided the total gas pressure is increased to maintain a constant oxygen partial pressure.

Figure 1 shows data from a laboratory study in which oxygen purities between 60% and 80% were used to delignify pulp. At constant total gas pressure and operating conditions, the amount of delignification dropped with the drop in purity. However, when the total gas pressure was increased to maintain constant partial pressure, the amount of delignification remained constant.

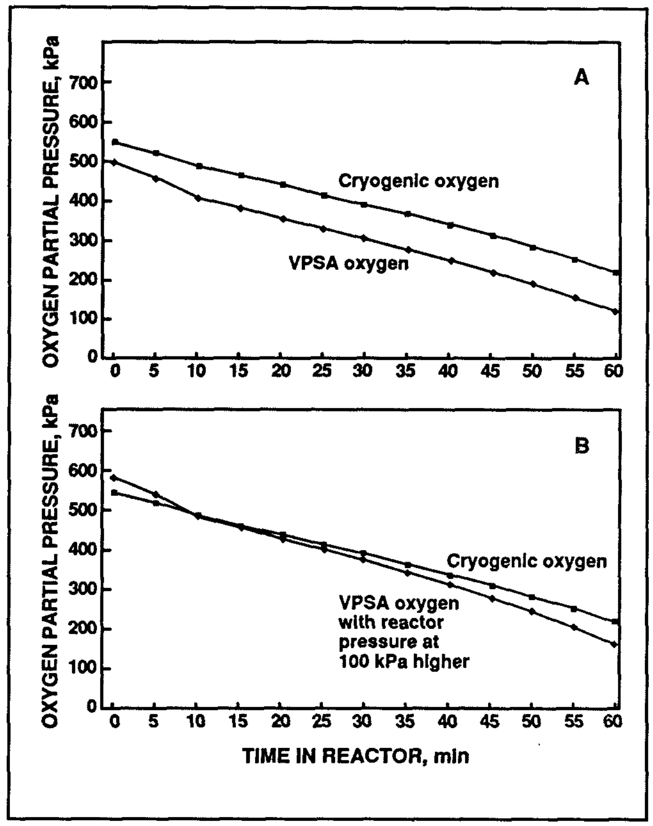
Figure 2A shows how the partial pressure of oxygen in a delignification stage varies with time as the pulp travels up the reactor. The upper line shows pure oxygen; the lower line shows 90% pure VPSA oxygen.

Figure 2B shows the expected result when the reactor pressure is increased by 100 kPa (14 psi). From this result, it appears that a modest increase in reactor pressure can compensate for the lower purity.

Gas volume

Oxygen reactors are designed to provide enough retention time for the oxygen to react with the pulp. If VPSA oxygen is used in place of cryogenic oxygen, the extra inert gas will occupy volume in the reactor and reduce the retention time. At a typical reactor operating pressure of 550 kPa (80 psig) at the bottom and 275 kPa (40 psig) at the top, the inert gas in an oxygen dose of 25 kg/a.d. metric ton is equal to 3% of the pulp volume at the bottom and 5% at the top.

2. A: With the same reactor pressure, the oxygen partial pressure is lower with the 90% pure VPSA oxygen. B: The oxygen partial pressure is corrected by raising the reactor pressure when using VPSA oxygen.



In the worst case with no pressure compensation, the tower retention will be shortened by 3-5% by an oxygen dose of 25 kg/a.d. metric ton. This effect can be lessened by increasing the tower back-pressure.

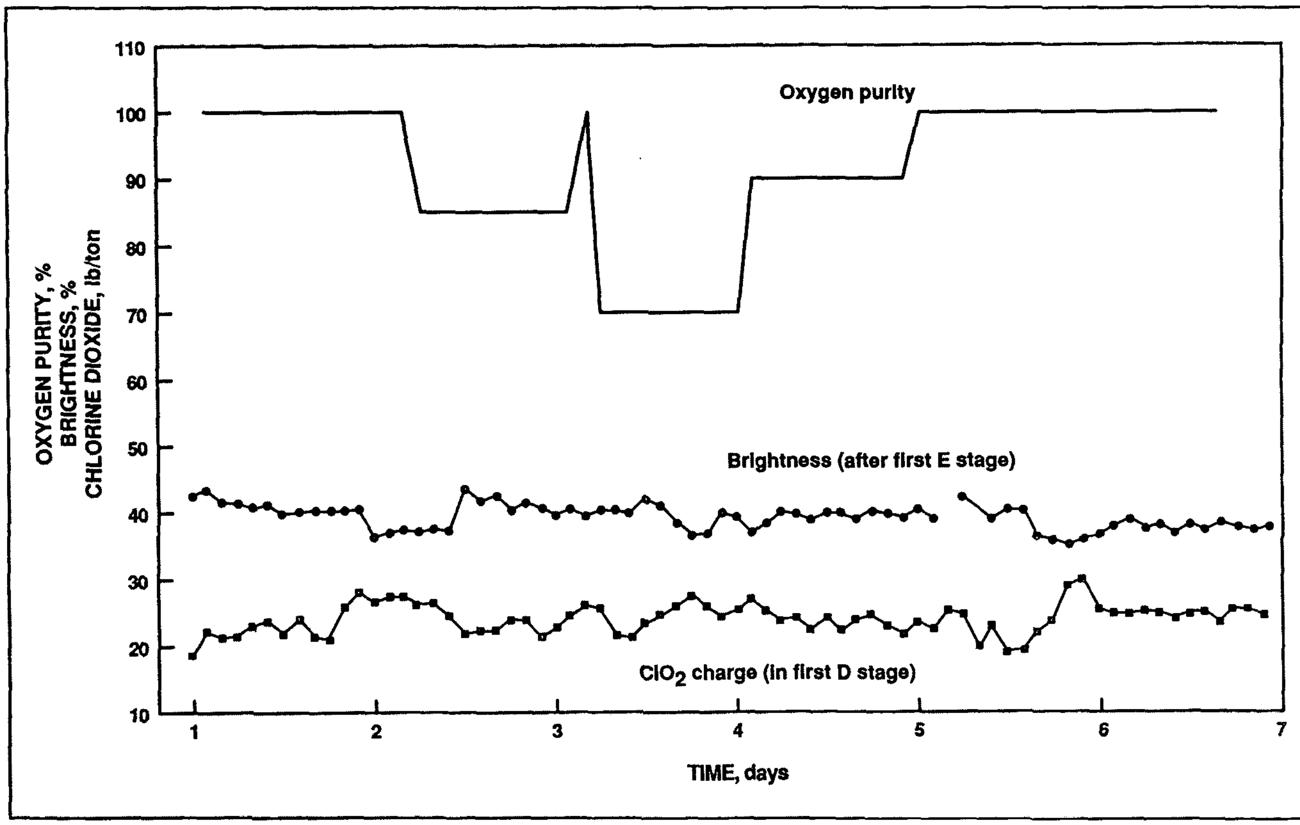
Another possible effect of the extra gas volume is channeling. Oxygen reactors are prone to channeling, and extra gas volume mixed with the pulp may make this problem worse. By increasing the back-pressure by 10%, the volume of VPSA oxygen entering a reactor can be reduced to the same volume as cryogenic oxygen. However, when the gas reaches the top of the reactor, most of the oxygen will have been consumed. A VPSA bubble will have roughly 1.5 times the volume of a cryogenic bubble when 90% of the oxygen is consumed from both, though the bubble is one third its original volume. This bubble may cause a problem in the upper section of the reactor, although it does not seem likely.

Post-oxygen washing

Most pulp washers or presses are adversely affected by large amounts of air trapped in the pulp. The entrained air inhibits drainage and the effective displacement of spent liquor, thereby increasing chemical carryover. The concern with VPSA oxygen is that the inert gas added with the oxygen (primarily nitrogen and argon) will remain trapped in the pulp after the oxygen stage and will affect the post-oxygen washing.

The maximum oxygen dose that will be used in an oxygen delignification stage is 2.5% on pulp, which is 18.5

3. Brightness and chemical consumption during the trial with oxygen of low purity



m^3 of gas at atmospheric temperature and pressure per metric ton of pulp. If the amount of inert gas is 10% of the oxygen dose, or 1.85 m^3, then the volume of the inert gas at atmospheric pressure is equal to 18.5% of the volume of the pulp at 10% consistency or 6.5% of the pulp volume at 3.5% consistency. If all this gas remained in the pulp, it would cause problems with most types of washers.

It is unlikely that the inert gas bubbles remain in the pulp. The physical action of blowing the pulp causes rapid expansion of the gas and high turbulence that releases the gas. In addition, the rapid drop in pressure from inside the reactor (200 kPa or more) to the blow tank at atmospheric pressure causes the hot pulp to flash steam. Even at the mild discharge conditions of 200 kPa and 90°C, the quantity of steam flashed will be greater than twice the volume of the residual gas. The quantity of steam increases rapidly as the temperature increases (5 times at 95°C). The steam generated will help in stripping residual gases from the pulp. Finally, most installations incorporate a degassing system such as a cyclone separator or a splash plate.

Oxygen in excess of the stoichiometric requirement is added to most oxygen delignification stages. The blow tanks can handle this excess gas. The behavior of inert gas should not be much different.

Summary

Based on the theoretical evaluation of the three potential problems, the use of VPSA oxygen in the 90–93% purity range should not cause a mill serious problems. A modest increase in the pressure of the oxygen reactor should compensate for any reduction in performance. The only delignification reactors that might have problems with VPSA oxygen are those that are operating at maximum capacity and pressure, with cryogenic oxygen, to get good results.

In light of this evaluation, two mill trials were carried out to test the effect of VPSA oxygen purity on an oxygen delignification stage.

Mill Trial 1

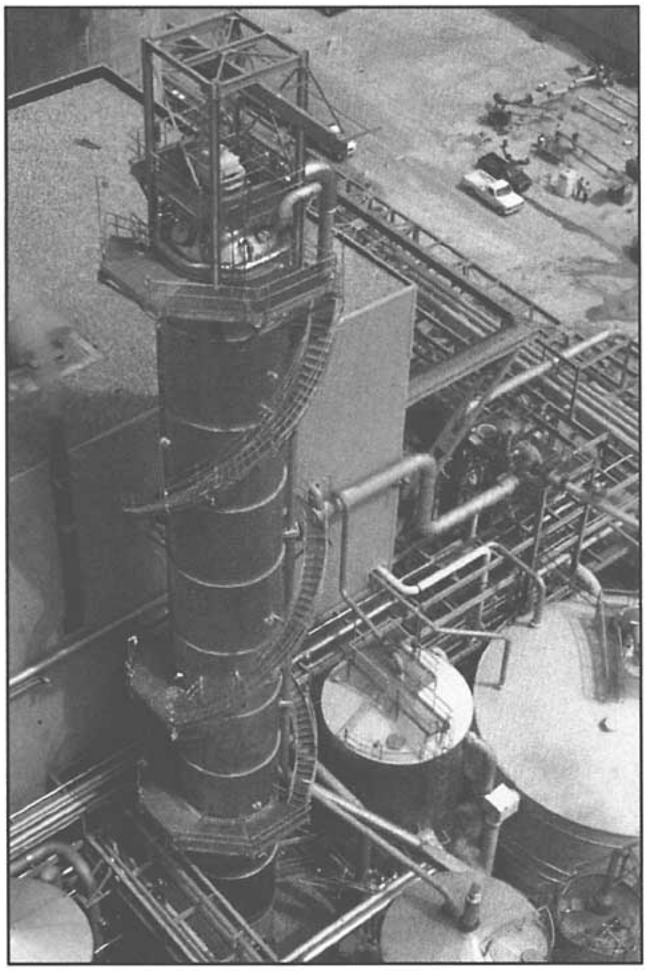
The first mill trial of VPSA-purity oxygen was run at Weyerhaeuser Canada's pulp mill in Kamloops, B.C. In this case, an oxygen extraction stage was used to model a medium-consistency oxygen delignification stage. The key parameter studied was the post-oxygen washer.

The mill

Weyerhaeuser Canada Limited's pulp mill in Kamloops, B.C., produces fully bleached market kraft pulp. In the bleach plant, up to 1000 tons/day of softwood chip pulp are bleached with a CD(E+O)DED sequence.

The (E+O) stage was the first installed in Canada and was started up in 1978. It operates at an initial temperature of 82°C and a vat pH of 10.5. It incorporates a high-shear oxygen mixer that is the prototype of the Beloit mixer. The Kamloops mill's mixer does an excellent job

4. The oxygen delignification stage at Weyerhaeuser, Columbus



I. Delignification results, VPSA vs. cryogenic

	Cryogenic	VPSA
Kappa reduction, %	33.4	31.6
Reduction in kappa no./oxygen dose	6.3	6.1
Channeling	Moderate	Moderate
Post-oxygen wash press	1.9	1.8
Vat gas content		
Chemical carryover		
COD, kg/a.d. ton	11.7	13.2
Sulfate, kg/a.d. ton	2.9	3.3

The operation of the post-oxygen wash press was not affected by the type of oxygen.

of blending oxygen into pulp. The extraction stage is an upflow-downflow design. It has a pre-retention tube with 1-1.5 min of retention. This time is much shorter than the conventional 5-10 min that most mills have, and Weyerhaeuser compensates by pressurizing the tube to 200 kPa (30 psig) at the discharge.

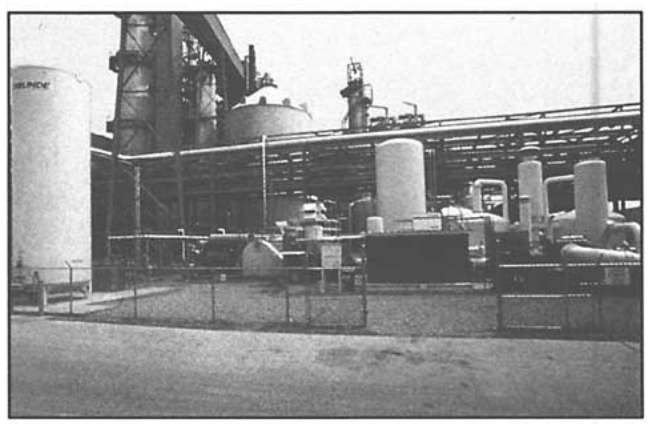
The combination of excellent mixing and pressurization produces good results, although the oxygen addition rate is higher than normal at 7.5 kg/a.d. metric ton (15 lb/ton), versus a typical rate of 5 kg/a.d. metric ton (10 lb/ton). Kappa number reduction and chemical savings from the addition of oxygen are comparable to other successful (E+O) installations. (Since the trial, the (E+O) stage has been modified to give more pre-retention time.)

The extraction stage washer is 4.1 m (13.5 ft) in diameter by 9.1 m (30 ft) long. It processes 1000 metric tons/day. The vat consistency is about 1.7% (air-dried pulp), and the repulper consistency is about 11% (air-dried pulp). The shower flow is 6250 L/min (1650 gal/min), which gives a wash ratio of 1:1.1.

The pulp is blown from the pre-retention tube through a 15-cm (6-in.) control valve into the top of the extraction tower that has roughly 1 h of retention before the pulp is diluted and pumped to the extraction washer.

Oxygen for the (E+O) stage is provided from an on-site cryogenic storage system. Commercial-purity oxygen (99.5%) is trucked from merchant plants.

5. The VPSA plant at Weyerhaeuser, Columbus



The Kamloops mill was a good test case because the configuration of the (E+O) stage (a pressurized reactor that blows into a large vessel) approximates the configuration of a typical oxygen delignification stage. This arrangement is useful to test the ability of the pulp to de-gas when blown from a reactor. The arrangement would tend to be less effective than a commercial medium-consistency oxygen delignification stage. It does not incorporate a degassing device (a cyclone or splash-plate, for example),

II. Reduction in kappa number, VPSA vs. cryogenic oxygen

	Cryogenic			*VPSA*		
	Avg.	*Std. dev.*	*Max. value*	*Avg.*	*Std. dev.*	*Max. value*
Kappa number						
Before oxygen	25.2	3.4	33.9	27.3	4.1	34.8
After oxygen	16.6	2.5	22.6	18.5	3.0	23.9
O_2 dose, % on pulp	1.39	0.22	1.8	1.44	0.17	2.0
Reduction						
Kappa points	8.54	3.0	15.7	8.75	3.2	14.4
Percentage, %	33.4	9.6	53.0	31.6	9.4	50.0
Points/% O_2 dose	6.3	2.4	14.0	6.1	2.4	12.9

Based on 70 samples for cryogenic and 44 samples for VPSA.

which most medium-consistency oxygen delignification stages have. Furthermore, it operates at a lower temperature (70°C vs. 90°-100°C) and will not flash as much steam to strip the residual gases.

The (E+O) stage

The oxygen dose used in the Kamloops (E+O) stage is lower than the dose used in typical oxygen delignification stages: 0.75% vs. 2.5%. To add an equivalent amount of inert gas relative to the pulp, the oxygen purity would have to be 70% to correspond to 90% in a medium-consistency oxygen delignification stage.

Low-purity oxygen used in the trial was produced by blending nitrogen with the cryogenic oxygen. The use of nitrogen only instead of nitrogen and argon as the inert component was not expected to be relevant. Oxygen purity as low as 70% was produced. The gas flow rate to the (E+O) stage was adjusted to maintain a constant quantity of contained oxygen.

The performance of the (E+O) stage was evaluated by examining the bleach plant logs and through discussions with the operators. The gas content of the pulp in the extraction stage vat and the filtrate was measured with an entrained gas tester, which measures the compressibility of a sample and relates this to gas content. The accuracy of this device depends on careful use and calibration. However, the reproducability of the test was good to within ±0.5%. The results provide a good relative comparison.

Results

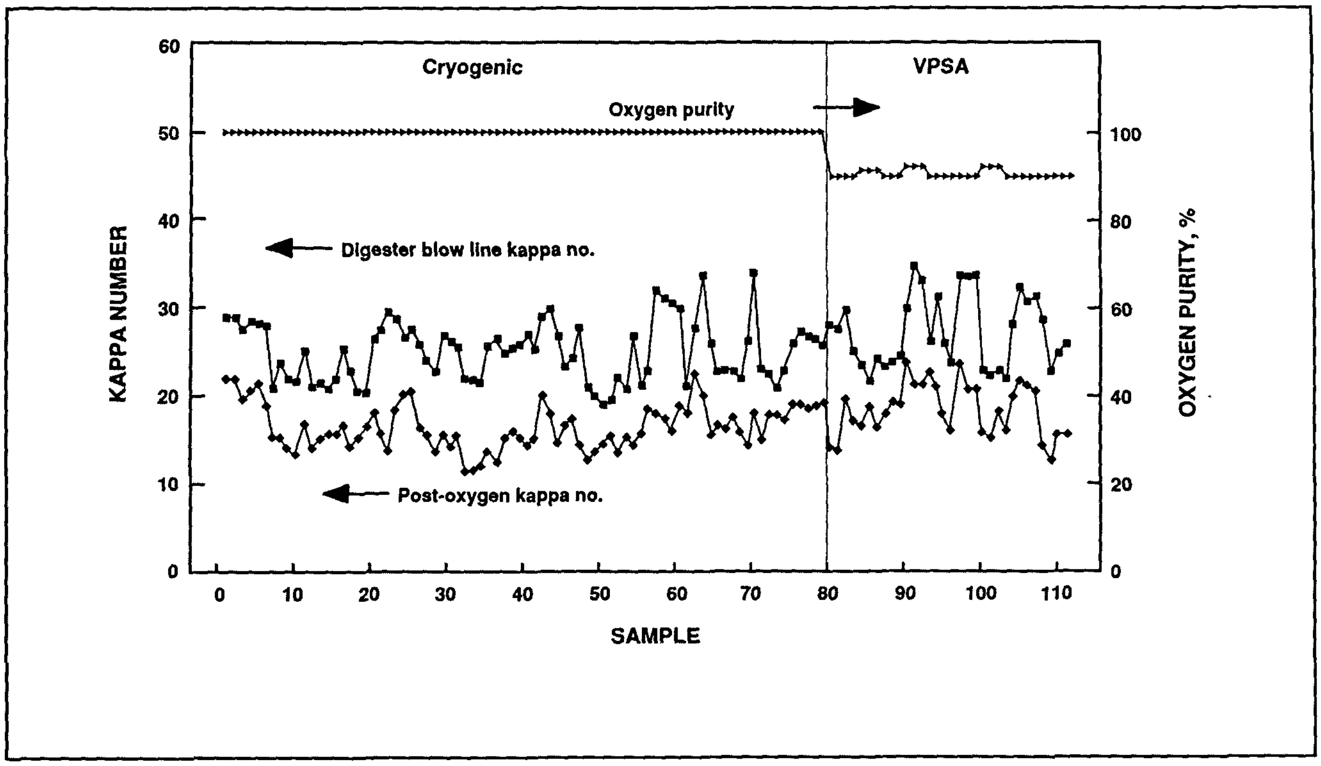
The trial ran for a week and a half. Examinations of the daily logs for chemical consumption and brightness (after caustic extraction) showed no discernible effect. **Figure 3** shows the brightness and chemical consumption in the first delignification stage during the period when low-purity oxygen was used. Operators and managers could not tell when low-purity oxygen was being used, even during a 20-h period when 73% oxygen was used.

The gas contents of the pulp in the washer vat and the filtrate in the washer seal tank were not affected. The gas content was somewhat high—between 4% and 6% in the vat and 2% and 4% in the seal tank—even with pure oxygen. The use of the oxygen of lower purity did not cause any additional problems.

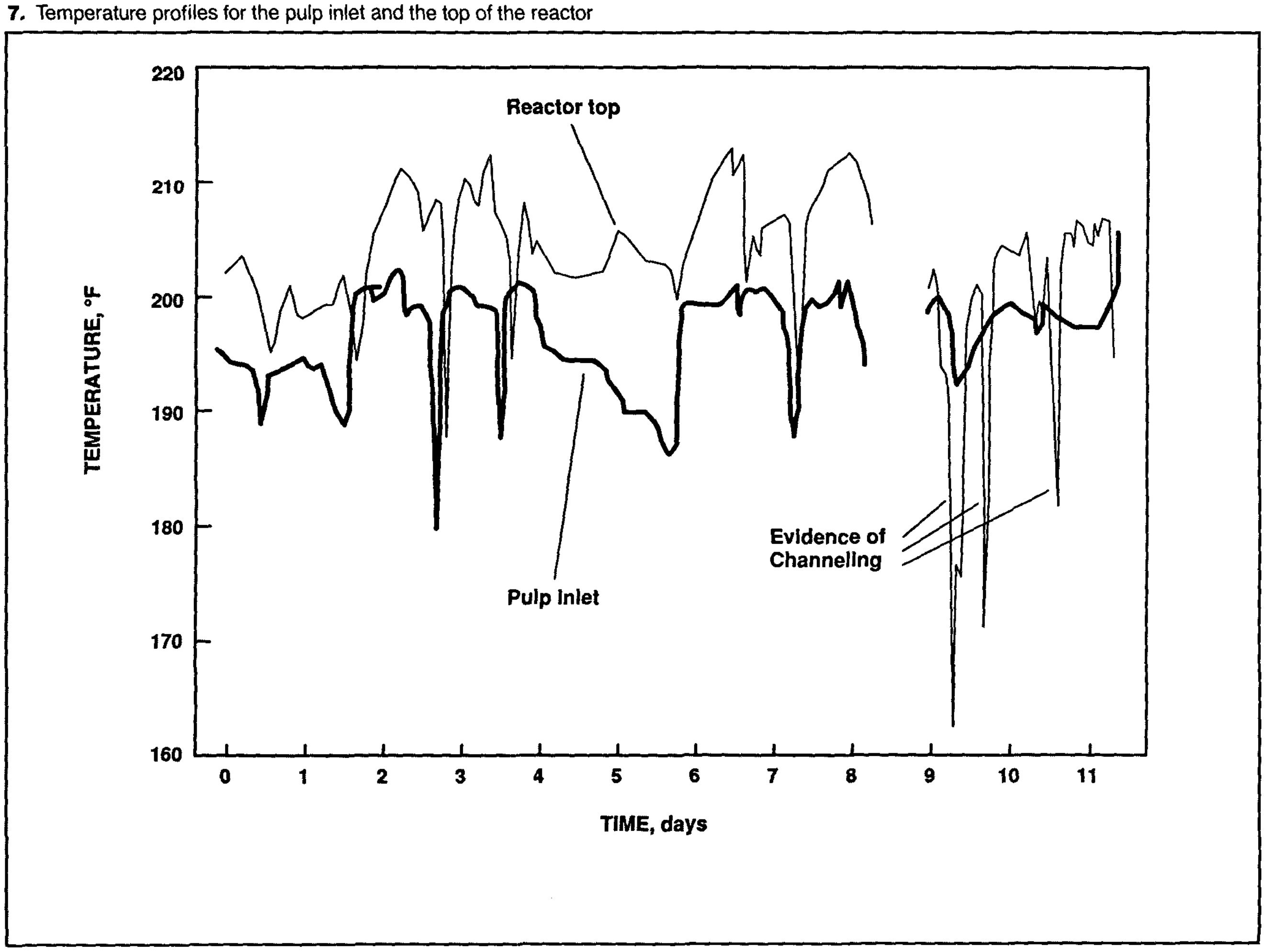
Mill Trial 2

The second trial was carried out at Weyerhaeuser's pulp and paper complex in Columbus, Miss. In this case, an oxygen delignification system was changed from cryogenic oxygen to VPSA oxygen.

6. Kappa numbers in the digester blow line and after oxygen. The VPSA oxygen begins where the oxygen purity drops to 90%.



7. Temperature profiles for the pulp inlet and the top of the reactor



The mill

Weyerhaeuser's Columbus mill has been supplied with oxygen from a commercial VPSA plant since July 1990. In 1990, a new kraft mill was started at the site. This mill was designed to produce 1200 a.d. tons/day of fully bleached softwood kraft from Southern pine. The mill incorporates a Kamyr MCC continuous digester, Sunds knotters and screens, a Sunds decker and displacement press for brownstock washing, and a Sunds medium-consistency oxygen delignification system followed by two displacement presses. A Kamyr diffusion washer bleach plant runs a (C75+D25)(E+O)(DN)D sequence. **Figure 4** is a photo of the oxygen delignification stage.

During the relatively smooth mill startup, the mill used cryogenic oxygen from a bulk storage tank. The VPSA plant was started in July 1990. It produces up to 41 metric tons per day of 90% oxygen and incorporates the latest design features, including a two-bed design, vacuum sieve regeneration, and a patented advanced absorbent. The plant is built, owned, and operated by Union Carbide, Linde Division. **Figure 5** is a photo of the VPSA plant.

During the conversion from cryogenic to VPSA oxygen, the mill was monitored closely to see if any problems arose. For a seven-day period, the mill alternated between VPSA and cryogenic oxygen to see if any trends developed.

The only adjustment made for VPSA oxygen was to increase the gas flow rate to compensate for the inert gas component and to maintain a constant contained oxygen flow rate. The tower back-pressure was not adjusted to compensate for lower partial pressure, nor were the temperature and caustic charge varied. All chemical doses were set by the operators according to guidelines in the mill operating procedures.

Results

The results obtained during the trial are summarized in **Table I**. These results pertain to the performance of the oxygen delignification stage only. [Note: The mill also operates an (E+O) bleaching stage. The performance of the (E+O) stage was not discernibly affected by the use of VPSA oxygen.]

Delignification

The delignification results with the two types of oxygen were similar. **Figure 6** shows the digester blow line and post-oxygen kappa numbers during the trial period. Data collected during startups and upsets were discarded.

Table II compares delignification achieved with VPSA oxygen and with cryogenic oxygen under normal operating conditions. The most important parameter is the number of points of kappa number reduction per percent oxygen dose added. The value was 6.3 points for cryogenic oxygen as opposed to 6.1 points for VPSA oxygen. This difference is not statistically significant, given the short period during which the VPSA was used.

The average amount of delignification during the trial period was somewhat low—a mean of 31.6% with VPSA oxygen and a mean of 33.4% with cryogenic oxygen. This average was all the operators were looking for to meet their targets. In spite of the low average, the system did achieve 50% delignification several times with VPSA oxygen.

In summary, it appears that the bleaching performance with VPSA oxygen was the same or very close to that achieved with cryogenic oxygen, even with no compensation for pressure. As the mill operates for a longer period with VPSA oxygen, the exact values will be determined.

Channeling

The reactor experienced occasional channeling during the trial period. Channeling shows up as a low temperature at one of the reactor temperature indicators, located at the bottom, middle, and top of the reactor. Immobile pulp along the reactor wall cools and then insulates the temperature indicator from the hot pulp in the center of the reactor. The reactor is designed to have a 1-h retention time. If channeling became severe, the retention time may become less than necessary for the oxidation reaction to occur.

Figure 7 shows the temperature at the top of the reactor and the temperature of the incoming pulp. The temperature at the top should be higher because of the exothermic oxidation reaction. Occasionally, toward the end of the trial, it dips below the incoming pulp temperature, indicating that channeling is taking place. **Figure 8** shows periods when channeling was occurring. This period includes time when the top temperature was less than the incoming pulp temperature plus an extra two hours before. It is assumed that the pulp was channeling during the extra two hours but had not yet cooled. Figure 8 also shows when VPSA oxygen was in use. The two are not related. Any channeling that occurred at the bottom or middle of the reactor was similarly unrelated to the use of VPSA oxygen.

Operators cleared channeling by varying the reactor discharge pressure. They stated that channeling was no more frequent using VPSA oxygen and no more difficult to clear. The cause of the channeling was attributed to the low consistency of the pulp entering the reactor.

Post-oxygen washing

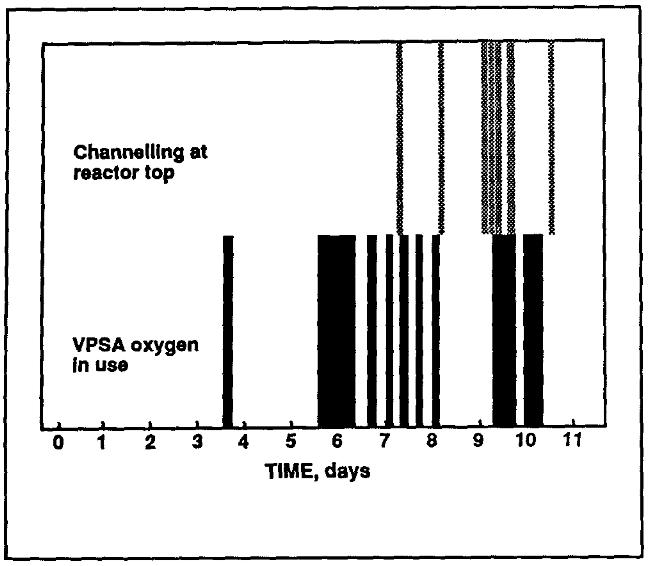
The Sunds displacement press located immediately after the oxygen blow tank was monitored to see if there were any adverse effects due to the VPSA oxygen. Roll speed, roll pressure, and vat pressure showed no discernible effect, as **Fig. 9** shows.

Three measurements were made of the press discharge consistency during periods when VPSA oxygen was being used. These showed normal values (33.9%, 32.5%, and 33.5%).

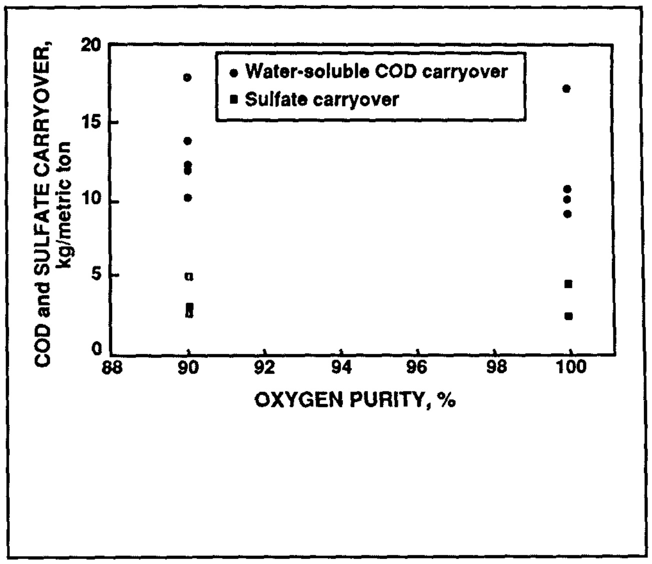
The gas content of the pulp entering the press was monitored. A sample of the stock (of 3.5% consistency) was drawn from the line feeding the press vat. The weight of this sample was compared with that of a sample of degassed filtrate, using a manometer. The difference in weight corresponds to the gas trapped in the stock. Throughout the trial, the gas content was between 1.0% and 2.5%, for all purities between 90% and 100%. Samples from the other presses showed similar values.

As a final check, samples of washed pulp produced during periods when the mill was using VPSA oxygen and cryogenic oxygen were sent for analysis to compare press performance. Soluble COD and saltcake carryover were measured. The results are presented in **Fig. 10** and do not show any appreciable correlation to oxygen purity. They do appear to be correlated to pulp production rate, as shown in **Fig. 11**.

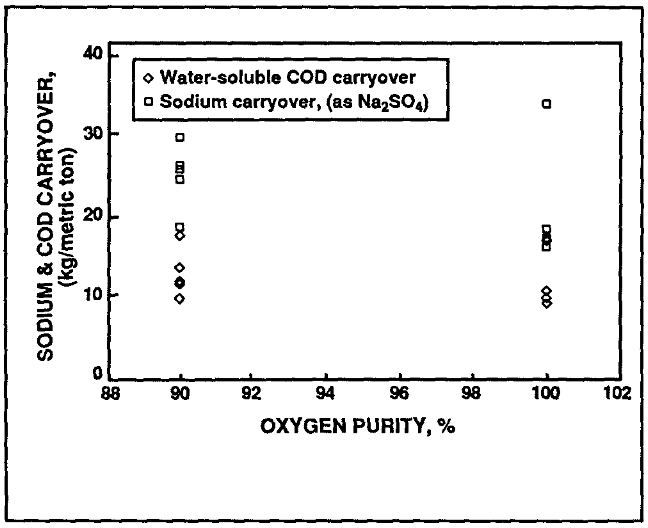
8. Periods when channeling was occurring in oxygen reactor did not correspond with periods during which VPSA oxygen was in use.



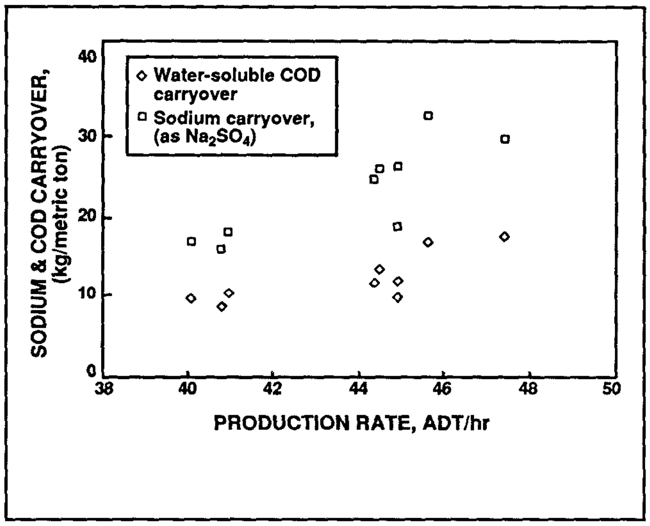
9. Post-oxygen displacement press, showing roll speed, roll pressure, and vat pressure



10. Post-oxygen wash press performance, showing chemical carryover and oxygen purity



11. Post-oxygen wash press performance, showing chemical carryover vs. pulp production rate



Conclusions

VPSA oxygen that is 90-93% pure can be used for oxygen delignification without any adverse effects. This process should be considered for mills that have a requirement for oxygen. The theoretical evaluation indicated that a marginally higher operating pressure may be necessary with VPSA oxygen. However, the mill trials showed no need to operate at a higher pressure.□

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The authors would like to express their thanks to the operators, technicians, and maintenance people in the Columbus and Kamloops mills, who were extremely helpful during the trials. Special thanks to Weyerhaeuser management, which supported the test work.

Received for review July 31, 1990.

Accepted Nov. 21, 1990.

Presented at the TAPPI 1990 Oxygen Delignification Symposium.